Chapter

Advanced Oxidation Processes (AOPs) – Utilization of Hydroxyl Radical and Singlet Oxygen

Pavel Krystynik

Abstract

Considering the nature of organic contaminants in water, methods of their oxidative decomposition seem to be most appropriate for their removal from contaminated water. There are a lot of methods of chemical oxidation, however, Advanced Oxidation Processes (AOPs) seem to be the most suitable technologies for organic contaminants removal. AOPs belong to a group of processes that efficiently oxidize organic compounds towards harmless inorganic products such as water or carbon dioxide. The processes have shown great potential in treatment of pollutants of low or high concentrations and have found applications for various types of contamination. The hydroxyl radical (•OH) is oxidizing agent used at AOPs to drive contaminant decomposition. It is a powerful, non-selective chemical oxidant, which reacts very rapidly with most organic compounds. Another strong oxidizing agent, singlet oxygen, can be generated by photosensitization of phthalocyanines. Phthalocyanines are molecules based on pyrrol structures connected mainly with methionine groups (–CH=) having a metallic central atom. Illumination upon specific wavelengths initiates formation of singlet oxygen that attack organic contaminants.

Keywords: hydroxyl radicals, singlet oxygen, advanced oxidation processes, photosensitization, oxidation

1. Introduction

Considering the nature of contaminants, chlorinated hydrocarbons and other groups of organic compounds belong to the group of chemicals that have widely been used in the past due to their environmental persistence and toxicity their use has been prohibited and became greatly controlled. [1–7] They can be decomposed by many chemical oxidation processes among which Advanced oxidation processes (AOPs) prevail. AOPs represent a group of methods of chemical oxidation in liquid phase which are employed to destroy organic compounds. AOPs were developed in order to oxidize organic compounds that can be resistant or which are able to deactivate traditionally used biological stage at sewage disposal plants (these compounds are non-biodegradable) including also pharmaceutical residues. [8, 9] If the final results of chemical oxidation are just inorganic products, such as CO_2, H_2O and other harmless inorganic compounds, we talk about complete mineralization or total oxidation. AOPs are employed to replace standard oxidation technologies, such as oxidation with $KMnO_4$, $K_2Cr_2O_7$ and $Na_2S_2O_8$ because they can oxidize many

organic compounds only partially. [10] Those oxidants can also serve as secondary source of pollution, e.g. hexavalent chromium ions are environmentally non-friendly. Some of the AOPs can also be based on sulphate chemistry combined with UV irradiation or photochemical processes combined with electrochemical processes. [11, 12] The effectiveness of oxidation agents is given by their standard oxidation potentials that were listed in **Table 1** in Section 2.1.3. AOPs comprise several common features that can be briefly described as follows: [13–17].

- Hydroxyl radicals OH• are employed as reactive oxidizing agent without any restrictions to reaction mechanisms.
- OH• attack is very fast; Rate constant reaches values of 10^9 mol^{-1} dm^3 s^{-1}.
- OH• attack reveals very low selectivity; It gives very high assumption for wide utilization of AOPs for water treatment containing non-biodegradable organic compounds.
- AOPs can effectively work at ambient pressure and temperature; It brings savings in process cost.
- OH• can be generated by various methods; It gives flexibility to utilization of AOPs for solving of various practical problem.

The main disadvantages of AOPs are relatively high treatment costs and special safety requirements because of the use of very reactive chemicals (ozone, hydrogen peroxide), etc. and high-energy sources (UV lamps, electron beams, etc.). Attention is also paid to low energy sources, such as UV LED. [18] Among AOPs the following processes can be categorized: Fenton oxidation (Fe^{2+}/H_2O_2); Fenton-like oxidation (Fe^{3+}/H_2O_2); photo assisted Fenton ($Fe^{2+/3+}/H_2O_2/UV$); photocatalysis (TiO_2/hv/O_2); ozone systems (O_3/H_2O_2, O_3/UV), UV photolysis (UV/H_2O_2). It is favorable to treat wastewaters with maximum content of COD = 10 to 15 g/L (chemical oxygen demand). [19] For higher values of COD, other oxidation methods are usually applied as can be seen in **Figure 1**.

Oxidative species	Reaction	E°[V]
Fluorine	$F_2 + 2H^+ + 2e^- \rightleftharpoons 2\ HF\ (aq)$	3.03
Hydroxyl radical	$OH• + H^+ + e^- \rightleftharpoons H_2O$	2.8
Singlet oxygen	$^1O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$	2.42
Ozone	$O_3 + 2H^+ + 2e^- \rightleftharpoons H_2O + O_2$	2.07
Sodium persulfate	$S_2O_8^{2-} + 2e^- \rightleftharpoons 2\ SO_4^{2-}$	2.01
Hydrogen peroxide	$H_2O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ H_2O + O_2$	1.78
Hydro peroxide radical	$2\ HO_2• + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ H_2O + O_2$	1.7
Potassium manganite	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	1.68
Chloride (IV) oxide	$ClO_2 + 4H^+ + 5e^- \rightleftharpoons Cl^- + 2H_2O$	1.57
Potassium dichromate	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O$	1.38
Chlorine	$Cl_2 + 2e^- \rightleftharpoons 2\ Cl^-$	1.36
Dissolved oxygen	$O_2\ (g) + 4H^+ + 4e^- \rightleftharpoons 2\ H_2O$	1.22

Table 1.
Standard redox potentials of some typical oxidative species [13].

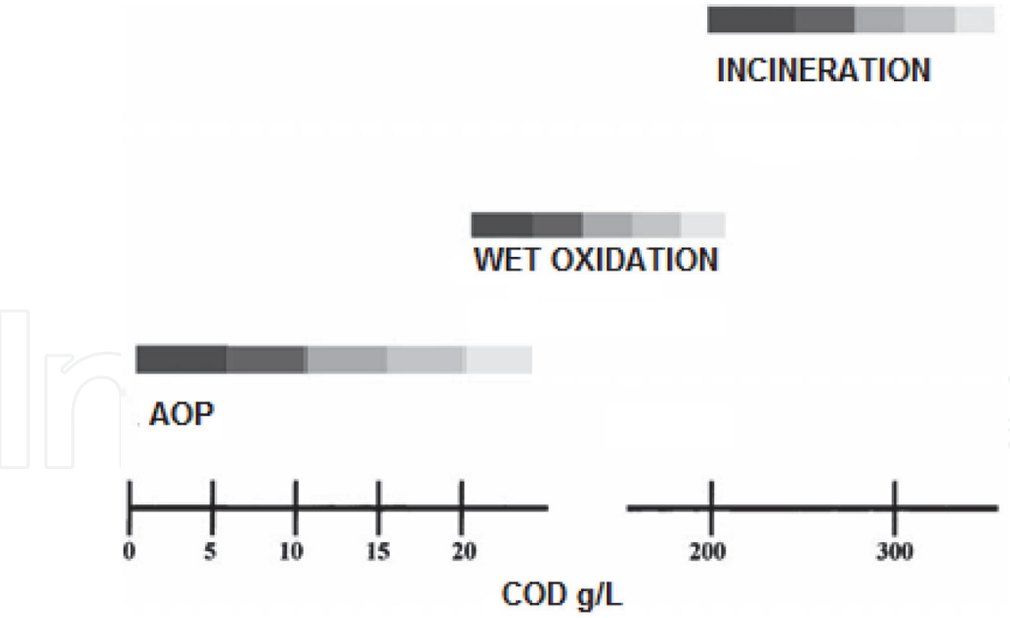

Figure 1.
Suitability of water treatment technologies according to COD contents [12].

Significance of the AOPs' usage in water treatment is supported by existing registered trademarks like ULTROX®, RAYOX®, UVOX®, ECOCLEAR®. Trademarks ULTROX®, RAYOX®, UVOX® are *ex-situ* water remediation technologies utilizing ultraviolet irradiation and ozone used by company Ultrox International in California, US. [20] ECOCLEAR® is a heterogeneous catalytic ozonation process. [21]

A brief summary of oxidative species used for chemical oxidation is briefly given in **Table 1**. The oxidative species are arranged according to their standard redox potentials. Standard redox potential describes capability of certain oxidizing agents for oxidation reaction. The higher the redox potential is revealed, the stronger the oxidizing agent is.

2. Fenton oxidation

Fenton oxidation is the most traditional method of AOPs. It was invented by Henry John Horstman Fenton in 1890. [22] He discovered oxidation with reagent containing Fe^{2+} and hydrogen peroxide. The OH• production occurs by means of H_2O_2 addition to the solution containing Fe^{2+} salts:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH\bullet \quad (1)$$

This is a very simple way of producing OH• requiring neither special reactants nor special reaction apparatus. Iron is naturally very abundant and non-toxic element to the environment. Hydrogen peroxide is also environment friendly chemical and easy to store and handle. It was pointed recently that at low values of pH = 2,5–3 Fe^{3+} salts are reduced to Fe^{2+} and reaction becomes Fenton-like. [23] It is described by Eqs. (2) and (3):

$$Fe^{3+} + H^2O^2 \rightleftharpoons H^+ + FeOOH^{2+} \quad (2)$$

$$FeOOH^{2+} \rightarrow HO_2\bullet + Fe^{2+} \quad (3)$$

Fenton oxidation also exists in several modifications. One of them is the photo assisted Fenton reaction. It is the classical Fenton reaction enhanced by presence of

UV–VIS irradiation. [24, 25] It utilizes a product yielding from reaction (2) and upon irradiation it yields Fe^{2+} ions and OH• as described by reaction (4).

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH\bullet \quad (4)$$

There are also other modifications of Fenton-like reactions, e.g. electro-Fenton, nano-Fenton utilizing graphene oxide wrapped nanoparticels of Fe3O4 [26, 27] and various modifications.

3. Photocatalytic processes

Photocatalytic processes employing semiconductor metal oxides have been the target of research interest for more than 30 years. [28] Many types of catalysts were tested and TiO_2 revealed many interesting properties (high stability, good performance and low cost) for organic compounds degradation. [29, 30] Triggering mechanism of TiO_2 photocatalysis is ultraviolet light absorption resulting in formation of electron–hole pairs.

$$TiO_2 + h\nu \rightarrow \bar{e} + h^+ \quad (5)$$

Electrons are capable of interaction with dissolved oxygen yielding superoxide radicals, and the holes are capable of oxidizing water molecules or hydroxyl anions adsorbed on the TiO_2 surface to reactive OH• radicals.

$$TiO_2\left(^{h+}\right) + H_2O \rightarrow TiO_2 + OH\bullet + H^+ \quad (6)$$

$$TiO_2\left(^{h+}\right) + OH^- \rightarrow TiO_2 + OH\bullet \quad (7)$$

Reactions 6 and 7 are of great importance in oxidative degradation of processes due to high concentration of H_2O and OH^- adsorbed on the catalyst surface. Great interest is also put on the exploitation of solar spectrum with TiO_2 but overlap between TiO_2 absorption spectra and solar spectrum is quite low. [31, 32] The emphasis is also laid on doping of TiO_2 with various metals. [33, 34] TiO_2 phtoocatalysis is also combined with SiO_2 or Al_2O_3 for enhancing photodegradability of organic compounds utilizing adsorption as synergistic effect. [35, 36]

4. Ozone water system

Ozone utilization for water purification is another well-known technology. [37] Ozone is understood as one of the most efficient oxidizing agents. As can be seen in **Table 1**, it is on the fourth position right after fluorine, hydroxyl radical and singlet oxygen. Ozone utilization can be intensified by addition of hydrogen peroxide and/or exploiting UV irradiation. Ozone water systems with H_2O_2 and/or UV require alkaline environment. [14, 16]

$$O_3 + H_2O + h\nu \rightarrow O_2 + H_2O_2 \quad (8)$$

$$2\,O_3 + H_2O_2 \rightarrow 2\,OH\bullet + 3\,O_2 \quad (9)$$

Another oxidation process utilizing ozone is $Mn^{2+}/(COOH)_2/O_3$ that is capable of hydroxyl radical production under gently acidic conditions (at pH > 4). Under

acidic conditions $Mn^{(III)}$ dioxalate and $Mn^{(III)}$ trioxalate are formed. Hydroxyl radicals are produced by reaction between manganese complexes and ozone. [16, 38] The decomposition of ozone is accompanied with hydroxyl radical generation and this decomposition is initiated by the presence of OH^-.

5. Hydrogen peroxide photolysis

Hydrogen peroxide photolysis by ultraviolet light (UV-C/H_2O_2) is one of the most effective AOPs. The UV-C/H_2O_2 system is based on the decomposition of hydrogen peroxide towards hydroxyl radicals using ultraviolet irradiation with wavelengths below 280 nm. [39] The mechanism of hydroxyl radical formation is understood as homolytic cleavage of hydrogen peroxide molecule yielding two radicals from one hydrogen peroxide molecule. On the contrary hydrogen peroxide has a small absorption coefficient (18.6 M^{-1} cm^{-1} at 254 nm) and consequently the utilization of UV-C light source is decreased when organic compounds act as optical filters[8]. The cage effect of water molecules also decreases the efficiency of hydroxyl radical generation. [15, 16] There are also studies reporting on hydrogen peroxide photolysis upon 308–465 nm. [40]

5.1 Hydrogen peroxide

It is a colorless, odorless, weakly acidic liquid similar to water having higher density and viscosity. It is miscible with water in all proportions. Hydrogen peroxide is a versatile oxidant that is effective over the whole pH range with relatively high oxidation potential (E_0 = 1.763 V at pH = 0, E_0 = 0.878 V at pH = 14) and water is the only co-product. [41]

Hydrogen peroxide can oxidize a broad variety of inorganic and organic substrates in liquid-phase reactions under mild reaction conditions. In industry H_2O_2 is used as an efficient bleaching agent in place of chlorine containing agents. Owing to its low molecular weight hydrogen peroxide is a more efficient oxidizing agent than other oxidants, such as nitric acid and sodium hypochlorite. H_2O_2 is an environment friendly compound since it decomposes towards water and oxygen (10). That makes it one of the cleanest and most versatile chemical oxidants available. [42] Hydrogen peroxide decomposition towards oxygen and water is intensified by increasing the temperature. Decomposition also occurs when hydrogen peroxide is exposed to metals.

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \tag{10}$$

The first historical preparation of hydrogen peroxide was performed by Luis Jacques Thenard in July, 1818. [43] In the 1950's production of hydrogen peroxide in industrial scale started to be performed by anthraquinone way. [44] The main stages of the process are (**Figure 2**):

- Hydrogenation of anthraquinone.
- Oxidation of the resulting anthraquinol.
- Extraction of hydrogen peroxide solution.
- Purification and concentration of hydrogen peroxide.

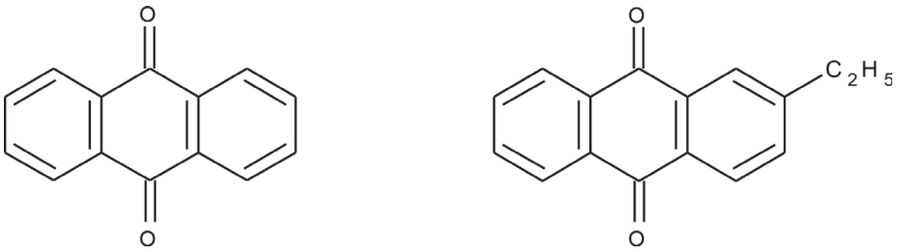

Figure 2.
Anthraquinone and 2-ethylanthraquinone.

The 2-ethyl derivate of anthraquinone is generally used in the process. A solution of the 2-ethylanthraquinone in a multi-compound mixed solvent system containing a non-polar hydrocarbons and polar solvents is hydrogenated using hydrogen. A suspension of a nickel or palladium based catalyst on a solid support is used. The reaction yields 2-ethylanthraquinol. Level of hydrogen feeding must be carefully controlled otherwise hydrogenation of aromatic rings occurs and undesired products are obtained. The catalyst is separated from the reaction mixture by filtration and it is recycled. The solution of 2-ethylanthraquinol is then oxidized by air to hydroperoxide, which reacts in water to reform 2-ethylanthraquinone and it produces a dilute solution of hydrogen peroxide. Thus the overall equation of hydrogen peroxide production is very simple:

$$H_2 + O_2 \rightarrow H_2O_2 \tag{11}$$

The demonstrative reaction scheme for anthraquinone process is shown in **Figure 3**: Illustrative reaction scheme of hydrogen peroxide production:

Water is added to extract the peroxide as an aqueous solution containing 35% w/w solution of hydrogen peroxide. The organic solvent layer is recycled to the hydrogenation unit for further reaction. The aqueous hydrogen peroxide solution is

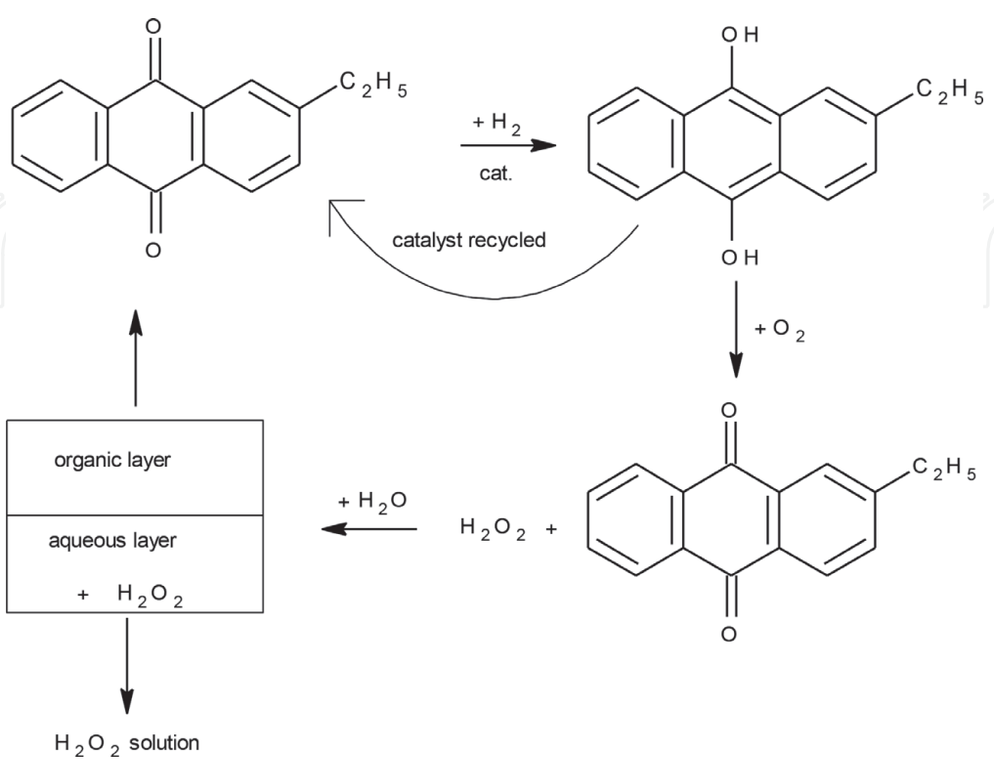

Figure 3.
Illustrative reaction scheme of hydrogen peroxide production from anthraquinone process [45].

treated with organic solvents and by air being pumped through to remove residual 2-ethylanthraquinone and solvents and produce the standard 35% product. Some applications require higher concentration product which is produced by vacuum concentration or distillation to concentrations of up to 70%.

Hydrogen peroxide in its purest form is inherently stable. However, if brought into contact with certain contaminants (mainly heavy metals) it can decompose according to Eq. (10). Typical additives enhancing stability of produced H_2O_2 are sodium compounds like stannate (IV) (which hydrolyzes to tin(IV) hydroxide), sodium citrate, sodium dihydrophosphate and various phosphates. [46] They act by complexing with any traces of transition metal ions present which would otherwise catalyze the decomposition of hydrogen peroxide. Acetone hydrogenation yielding propan-2-ol is an alternative to the use of 2-ethylanthraquinone. Oxidation of propan-2-ol yields hydrogen peroxide and acetone that is brought back to the beginning of the process.

5.2 Mechanism of hydrogen peroxide photolysis

The simplified mechanism of hydrogen peroxide decomposition is described as follows: [47].

$$H_2O_2 + h\nu \rightarrow 2\ OH\bullet \tag{12}$$

$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \tag{13}$$

$$HO_2\bullet + H_2O_2 \rightarrow OH\bullet + H_2O + O_2 \tag{14}$$

$$2\ HO_2\bullet \rightarrow H_2O_2 + O_2 \tag{15}$$

$$HO_2\bullet \rightarrow O_2^{\bar{\bullet}} + H+ \tag{16}$$

$$1/2\ O_2^{\bar{\bullet}} + H_2O \rightarrow H_2O_2 \tag{17}$$

$$1/2\ O_2^{\bar{\bullet}} + H_2O \rightarrow 2OH\bullet \tag{18}$$

The homolytic cleavage of hydrogen peroxide molecule yielding two hydroxyl radicals is described by Eq. (12). A certain part of hydroxyl radicals reacts with the hydrogen peroxide molecule yielding hydroperoxide radicals (Eq. 13). Hydroperoxide radical then reacts with hydrogen peroxide yielding the desired hydroxyl radicals (Eq. 14). Eq. (15) shows radical recombination that can lead back to the hydrogen peroxide. Also superoxide radicals can be produced from hydroperoxide radicals. Superoxide radicals can be then transformed into hydrogen peroxide or hydroxyl radicals in water environment (Eqs. 17 and 18). However, superoxide radicals appear in the reaction system utilizing hydrogen peroxide decomposition in much lower extent. [48, 49]

Hydroxyl radicals produced by reactions (12) to (14) can attack organic molecules and decompose them through various reaction intermediates towards inorganic products, such as CO_2, H_2O and relevant mineral acids. The formation of hydroxyl radicals increases when more alkaline conditions are used. Presence of hydroxyl anions causes formation of peroxide anion which reveals the molar absorption coefficient of 240 M^{-1} cm^{-1}. Photolysis of HO_2^- anions leads to additional formation of hydroxyl radicals. [50]

$$H_2O_2 + OH^- \rightarrow H_2O + HO_2^- \tag{19}$$

$$2HO_2^- + h\nu \rightarrow 2\ OH\bullet + O_2 \tag{20}$$

5.3 Reaction mechanism of hydroxyl radicals with organic molecules

The hydroxyl radical is a particle with very low lifetime period but very high reactivity. Mechanism of organic molecule attack is dependent on the type of organic molecule. In general, there are three possible simplified mechanisms: [13].

- Attack accompanied with hydrogen abstraction.
- Attack accompanied with electron transfer.
- Attack in terms of electrophilic addition.

The hydroxyl radical generated by direct hydrogen peroxide photolysis reacts with aliphatic organic compounds to produce an organic radical (R•). These radicals react quickly with dissolved oxygen yielding the organic peroxyl radical (RO_2•) initiating subsequent thermal oxidation reactions.

$$RH + OH\bullet \rightarrow H_2O + R\bullet TiO_2 + h\nu \rightarrow \bar{e} + h^+ \quad (21)$$

$$R\bullet + O_2 \rightarrow RO_2\bullet \quad (22)$$

Subsequent thermal reactions are of three types: [13, 51].

- Heterolysis and generation of organic cations as well as superoxide anion.
- 1,3-Hydrogen shift and homolysis into hydroxyl radicals and carbonyl compounds.
- Back reaction to R• and O_2.

The second mechanism of reaction is accompanied by electron transfer. Reduction of hydroxyl radicals to hydroxide anions by an organic compound is of particular interest in the decomposition of halogenated hydrocarbons.

$$RX + OH\bullet \rightarrow RX\bullet^+ + OH^- \quad (23)$$

The third possible mechanism is employed when organic molecules with multiple bounds react with hydroxyl radicals. This mechanism works either with aliphatic or aromatic hydrocarbons and runs similarly as electrophilic addition (**Figure 4**).

Electrophilic addition is of particular interest for an interpretation of the rapid dechlorination of chlorinated phenols yielding chloride ions. One possible pathway could in fact consist of an electrophilic addition of the hydroxyl radical to the aromatic ring and of subsequent fragmentation of the chlorohydrol intermediate followed by the ring opening (**Figure 5**).

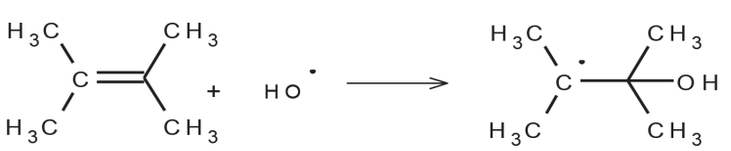

Figure 4.
Reaction scheme of electrophilic addition.

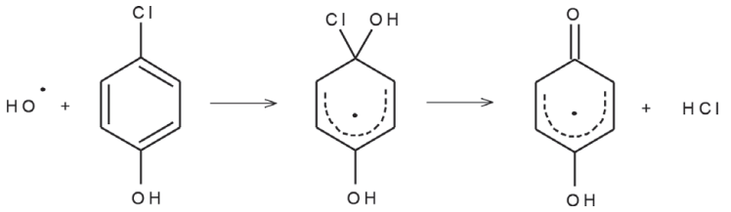

Figure 5.
Example of 4-chlorophenol attack with hydroxyl radical.

5.4 Advantages and limits

The use of hydrogen peroxide as an oxidant brings a number of advantages in comparison to other methods of chemical or photochemical water treatment: [14–16].

- Infinite solubility in water.
- No mass transfer problems associated with gases (for example ozonation).
- Two hydroxyl radicals are formed for each molecule of H_2O_2 photolyzed.
- Peroxyl radicals are generated after HO• attack on most organic substrates, leading to subsequent oxidation reactions.
- Minimal capital investment, very cost-effective source of hydroxyl radicals, and simple operation procedure.
- UV irradiation is capable of photolytic degradation of some compounds; Only addition of hydrogen peroxide leads to total oxidation.

There are, however, also obstacles encountered with the UV-C/H_2O_2 process: [52, 53].

- The rate of chemical oxidation of the contaminant is limited by the rate of formation of hydroxyl radicals.
- Molar absorption coefficient of H_2O_2 at 254 nm is only 18,6 $l \cdot mol^{-1} \cdot cm^{-1}$. It causes decrease of irradiation in cases where organic substrates act as inner filters.
- Higher rates of HO• radical formation may, nevertheless, be realized by the use of Xe-doped Hg lamps having a strong emission spectra in the region of 210–240 nm, where H_2O_2 reveals a higher molar absorption coefficient.
- Post-treatment of residual H_2O_2 might be required.
- UV light penetration is negatively affected by increasing turbidity.

The main disadvantage of oxidative processes using hydroxyl radicals as an oxidizing agents can be found in efficient trapping of HO• radicals by HCO^{3-} and CO^{3-} ions. [54] Hydroxyl radical is nonselective and, thus, can be exhausted by the presence of organic or inorganic compounds other than the contaminants of the main concern.

$$HO\bullet + HCO_3^- \rightarrow H_2O + CO_3^{\bullet-} \quad (24)$$

$$HO\bullet + CO_3^{2-} \rightarrow HO^- + CO_3^{\bullet-} \quad (25)$$

Carbonate and hydrocarbonate ions act then as scavengers of hydroxyl radicals. Similar observations were also made for ammonia. [55] Although, the generated carbonate radical anion has been shown to be an oxidant itself. Its oxidation potential is, however, significantly lower than that of the HO• radical. [56]

5.5 Reactors for UV-C/H_2O_2 oxidations

Most conventional UV reactors are often available in tubular arrangements and can either be an open channel or a closed vessel. [57] For large scale operation of these reactors, multistage arrangement (reactors in series) is recommended. [58] Ideal characteristic features of the tubular reactor arrangements are uniform flow through the inside of the reactor, high length-to-width ratio, flow from the bottom to the top[48]. Production of UV irradiation requires energy to supply UV lamps. Low and medium pressure mercury vapor lamps are considered to be the suitable option. [59] Another possible option is to use pulsed UV xenon arc lamps. [60] Low pressure lamps emit their maximum energy photons at wavelength of 254 nm, while medium pressure lamps emit photons with wavelengths ranging from 180 to 1370 nm with maximum between 200 and 400 nm. [61]

Typically, low-pressure lamps are closed in a quartz sleeve to separate the water stream from the lamp surface or alternatively the treated water can flow through the quartz tube surrounded by UV lamps. [62, 63] Although Teflon sleeves are also an alternative to quartz sleeves, quartz sleeves absorb only 5% of the UV radiation, while Teflon sleeves absorb 35%. [59] The UV lamps can be arranged in different ways in the reactor, depending on the required scale. A system designed for large scales (water flows over 1000 m^3/h), would typically consist of one single reactor vessel equipped with several UV lamps arranged perpendicularly or parallel to the water flow. [64] The more water needs to be treated, the more lamps and possibly more reactors in series are recommended. Generally, no or simple cooling system is required for systems handling large volumes of effluent, since heat transfers from the lamps are usually low (<1°C). [65]

Hydrogen peroxide introduction into the treated water is one of the most critical points of the oxidation process. It must not come to the contact with any metallic parts otherwise undesired decomposition of H_2O_2 is initiated. The reaction rate between hydrogen peroxide and organic compound determines the point of the H_2O_2 addition. [66] A good homogenization of reaction mixture must be ensured. The simplest method of hydrogen peroxide dosing is the gravity feed through mixing valve but this method is rather difficult to control the rate of dosing. Another easy option is the pump feeding which is very easy to maintain and to control the rate of hydrogen peroxide dosing. For water treatment 30–50% H_2O_2 solutions are recommended. Higher concentrations (≈ 70%) would increase the reaction rates, but these are not already safe because they can produce detonable mixtures upon storage. [67]

5.6 Perspectives of AOPs

Many AOP processes use UV radiation, but alone UV/O_2 photooxidation is generally effective when using ionizing (energy>5 eV) or polychromatic UV radiation. The energy of UV-A and UV-B radiation is for degradation of most organic substances by direct photolysis insufficient. The low-pressure mercury lamp is a

source of UV-C radiation with a wavelength of 253.7 nm, which is itself for removal most organic pollutants only partially effective. Therefore, this source is often combined with H_2O_2, O_3 and also with catalysts Fe^{2+}, Fe^{3}+ Mn^{2+} or TiO_2 in practice. The use of photolysis in application of polychromatic radiation, such as available medium-pressure mercury lamp (emitting radiation in the area 254–400 nm) can also be applied. This approach reveals advantages of both generations of radicals OH•, as well as for the direct excitation of organic molecules absorbing in UV region, such as benzene, toluene, xylene, dinitrotoluene or chlorophenols. However, the oxidation reaction rate of the pollutant tends to increase with increasing concentration of hydrogen peroxide, which is a source of OH radical. The H_2O_2 concentration must be carefully optimized because reaction system overdosed with H_2O_2 will result in undesired decomposition towards H_2O and O_2. Also, natural presence of scavenging ions may decrease applicability of the process.

6. Phthalocyanines

Phthalocyanines are macro-cyclic compounds that are derived from the group of heterocyclic compounds containing four pyrrol structures connected mainly with methionine groups (–CH=). A typical structure of metallic phthalocyanine is shown in **Figure 6**. Unlike porphyrines, phthalocyanines contain four benzene rings bounded on basic pyrrol structures. Phthalocyanines are, due to their photochemical properties, often labeled as photosensitizers. [68] Photosensitizers are compounds containing chromophores. Chromophore is a part of molecule responsible for light absorption. Absorption of light photon causes excitation to higher energy layer and reaction with molecular oxygen yields singlet oxygen species. [69]

It must be reminded that solubility of phthalocyanine in water is very low. Modification by halogenation, chlorine methylation, sulphonation or sulphochlorination influences their solubility in both polar and non-polar solvents. [70]

There are two major methods of phthalocyanine productions. The first is based on reaction of phthaloimide with relevant metal, metal chloride or metal alkoxide in quinoline solvent. Presence of urea enhances the reaction pathway with use of metal chlorides because it blocks chlorination of phthalocyanine structure. [71] Second method is based on the reaction of urea and phthalanhydride yielding di-iminophthaloimide. Di-iminophthaloimide then reacts with relevant metal chloride

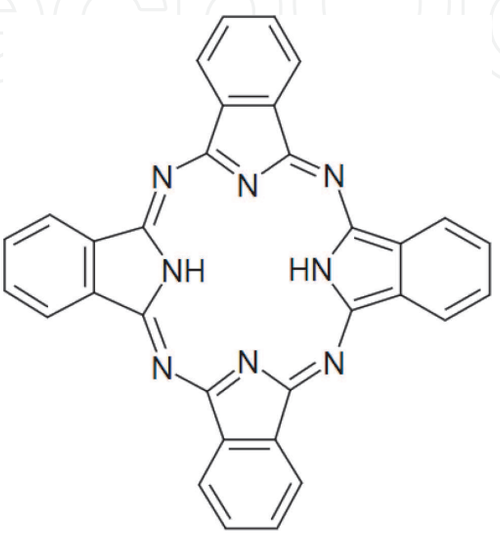

Figure 6.
Basic structure of the phthalocyanine molecule.

with sodium molybdate as catalyst. [72] First method is mostly performed as batch process; the second is carried out continuously.

Phthalocyanine produced by both batch and continuous methods reveals similar structure to the one showed in **Figure 6**. A characteristic metallic atom is bounded in the center of phthalocyanine molecule. However, as mentioned before, this raw phthalocyanine is insoluble in water. To enhance the solubility, benzene rings are modified by sulphonation or sulphochlorination. [70] The main area of phthalocyanine utilization covers dyes and pigments. Their share on the market is 30% of all produced organic dyes.

6.1 Mechanisms of singlet oxygen generation

It is known that phthalocyanines are capable to generate singlet oxygen when interact with visible light. [73] Singlet oxygen is a form of oxygen molecule in its excited state where all electrons are coupled. Singlet oxygen evinces high lifetime period. Stability of singlet oxygen species is dependent on reaction environment. [74]

The general mechanism of the phthalocyanine interaction with light is usually described by two types of reaction mechanisms. [75–77] For both mechanisms, interaction of phthalocyanine with visible light photons occurs, mostly at wavelength of 670 nm. **Figure 7** depicts absorption spectra of zinc phthalocyanine (ZnPC). Strong absorption area in visible part of spectra enables photon absorption followed by excitation. The double peak in visible area indicates a presence of both mono- and disulphonated forms of ZnPC. Absorption of photons at 670 nm causes excitation of phthalocyanine molecule towards the excited singlet state.

It starts with its absorption of photon(s) followed by intersystem crossing from the excited singlet state to the low-lying triplet state.

$$PC + h\nu \rightarrow {}^{1}PC* (isc) \rightarrow {}^{3}PC* \tag{26}$$

The triplet state of phthalocyanine transfers its energy to an oxygen molecule. The first mechanism involves hydrogen-atom abstraction or electron-transfer between the excited phthalocyanine and another molecule (e.g. solvent, air

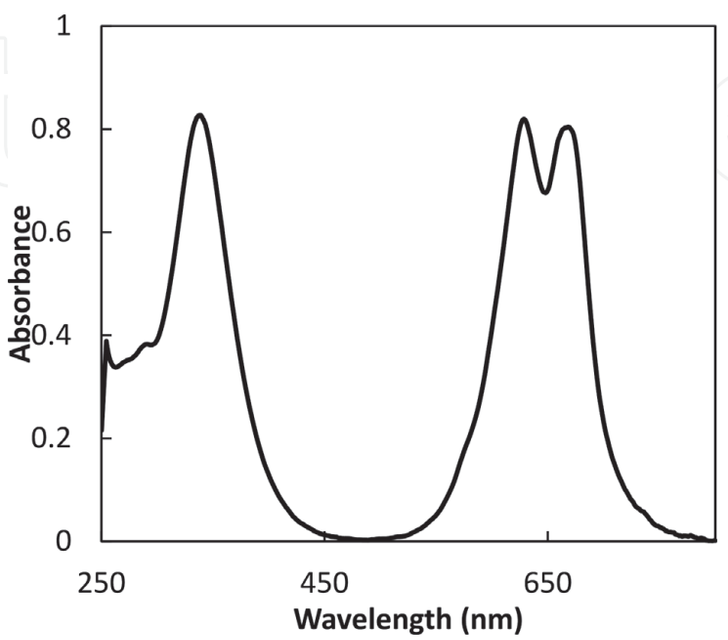

Figure 7.
Absorption spectra of ZnPC.

oxygen), forming free radicals and ion-radicals. [78, 79] These radicals can then react with ground-state oxygen to form an active species such as the superoxide radical anion.

$$^3PC* + O_2 \rightarrow PC^{\bullet} + O_2^{\bar{\bullet}} \quad (27)$$

$$PC^{\bar{\bullet}} + O_2 \rightarrow PC + O_2^{\bar{\bullet}} \quad (28)$$

$$½\ O_2^{\bar{\bullet}} + H_2O \rightarrow H_2O_2 \quad (29)$$

$$½\ O_2^{\bar{\bullet}} + H_2O \rightarrow 2\ OH^{\bullet} \quad (30)$$

$$O_2^{\bar{\bullet}} \rightarrow {}^1O_2 \quad (31)$$

This mechanism causes an electron transfer from phthalocyanine to oxygen molecule yielding superoxide anion-radical (Eqs. 27 and 28). Superoxide anion-radical tends to hydrogen peroxide formation in water environment and further produces hydroxyl radicals as active species (Eqs. 29 and 30) or it can be transferred towards singlet oxygen (Eq. 31). [80]

The second mechanism comprises interaction of triplet phthalocyanine state with molecular oxygen. Energy from triplet phthalocyanine transfers to the oxygen and the upcoming release of energy causes formation of singlet oxygen and basic state of phthalocyanine. [81]

$$^3PC* + O_2 \rightarrow PC + {}^1O_2 \quad (32)$$

6.2 Mechanisms of singlet oxygen interactions with organic molecules

As already mentioned singlet oxygen is a particle of long lifetime depending on the environment where it currently exists. And also the reaction mechanism depends on type of organic molecule which enters the reaction with singlet oxygen. It is supposed that singlet oxygen interacts with organic compounds upon yielding endoperoxides and superoxide radicals or hydrogen peroxide via mechanisms resulting in one- or two-electron transfer. [82]

In case of substituted aromatic hydrocarbon (e.g. 4-chlorophenol) chlorine cleavage can be observed yielding either *p*-benzoquinone or *p*-hydroquinone. Following reactions with singlet oxygen lead to aromatic ring opening (**Figure 8**).

6.3 Advantages and limits

The use of phthalocyanines as catalysts producing singlet oxygen reveals several advantages to other methods of chemical or photochemical water treatment: [83–86].

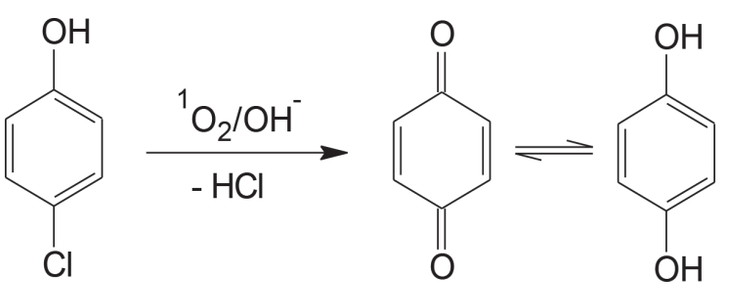

Figure 8.
Simplified reaction scheme of 4-chlorophenol attack by singlet oxygen.

- Thermal stability of the phthalocyanines.
- Solubility in water is possible to enhance by substitution of aromatic rings.
- No mass transfer problems.
- Possibility of artificial visible light utilization.

Difficulties related with the processes utilizing phthalocyanines as photosensitizers can also be found: [87].

- The rate of chemical oxidation of the contaminant is limited by the rate of formation of singlet oxygen.
- Crude form of phthalocyanine is insoluble in water thus modification has to be performed.
- Too high concentrations cause dark color of the treated water and light photons cannot reach the entire irradiated volume.

Phthalocyanine catalyzed oxidations have been widely described in the laboratory in cuvette arranged on optical bench. [88–90] Also performance of such catalyzed reaction in micro reactor arrangement is coming to the fore. [91, 92] Immobilization of phthalocyanines on various supports is also well known process but it does not work sufficiently. [93, 94] All these processes and many others are performed only at laboratory scale. First quarter scale experiments performed with phthalocyanines acting as photosensitizers have been described recently. [95] However, if the phthalocyanines successfully mineralize all organic contaminants in water, phthalocyanine removal needs to be applied as in treated water it would act as coloring contaminats. For such purposes, activated carbon might be effective.

7. Summary

Advanced oxidation processes for hydroxyl radicals and singlet oxygen species were introduced and discussed according to their mechanisms and applicability for water treatment. The emphasis was put on hydrogen peroxide photolysis in UV-C region but other AOPs were also introduced. Phthalocyanine utilization as photosensitizer for generation of singlet oxygen, as another strong oxidizing agent was also discussed. It has been demonstrated that applicability potential of such technologies exists. AOPs based on hydroxyl radicals' generation reveal higher potential for application because they usually don't require addition of coloring chemicals (as phthalocyanines).

Acknowledgements

Financial support of Technology Agency of the Czech Republic (Project No. SS02030008) and Ministry of Education, Youth and Sports of the Czech Republic (Project No. CZ.02.1.01/0.0/0.0/17_048/0007435) is gratefully acknowledged. Part of the work was provided by research infrastructure NanoEnviCz (Project No. LM2018124).

Conflict of interest

The author declares no conflict of interest.

Author details

Pavel Krystynik[1,2]

1 Faculty of Environment, University of J.E. Purkyne, Usti nad Labem, Czech Republic

2 Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Prague, Czech Republic

*Address all correspondence to: krystynik@icpf.cas.cz

References

[1] A. Moretto, Comprehensive Toxicology (Second Edition), Volume 13, 2010, 445-457.

[2] Tsygankov, V., Lukyanova, O., Boyarova M.: Marine Pollution Bulletin 2018, 128, 208-213.

[3] Campillo, J.A., Fernández, B., García, V., Benedicto, J., León, V.M.: Chemosphere 2017, 182, 584-594.

[4] Bapayeva G., Issayeva, R., Zhumadilova, A., Nurkasimova, R.: Reproductive Toxicology 2016, 65, 67-75.

[5] Muzyed, S. K. I., Kucuksezgin, F., Tuzmen N.: Marine Pollution Bulletin 2017, 119, 247-252.

[6] Trojanowicz M., Bojanowska_ Czajka A., Bartosiewitz I., Kulisa K.: Chem. Eng. J. 2018, 336, 170-199.

[7] Milun, V., Lušić, J., Despalatović M.: Chemosphere 2016, 153, 18-27.

[8] Taoufik N., Boumya W., Achak M., Sillanpää M., Barka N.: J. Environ. Manag. 2021, 288, 112404-112425.

[9] Rivero-Huguet, M.; Marshall, W. D. Chemosphere 2011, 83, 668-673.

[10] Siegriest R. L., Urynowicz M. A., West O. R., Crimi M. L., Lowe K. S.: Principles and practices of In situ chemical oxidation using permanganate. Battelle press, Columbus, Ohio 2001, ISBN-13: 978-1574771022.

[11] Ghime D., Ghosh P.: dvanced Oxidation Processes: A Powerful Treatment Option for the Removal of Recalcitrant Organic Compounds. InTech Open 2019. ISBN: 978-1-83880-971-3.

[12] Dewil R., Mantzavinos D., poulios I., Rodrigo M.A.: J. Environ. Manag. 2017, 195(2), 93-99.

[13] Dušek, L. Chem. Listy 2010, 104, 846-854.

[14] Badawya, M. I.; Ghalyb, Y.; Gad-Allaha, T. A. Desal. 2006, 194, 166-175.

[15] Legrini, O.; Oliveros, E.; Braun, A. M. Chem. Rev. 1993, 93, 671-698.

[16] Andreozzi, R.; Caprio, V.; Insola, A.; Marotta, R. Catal. Today 1999, 53, 51-59.

[17] M'Arimi M.M., Mecha C.A., Kiprop A.K., Ramkat R.: Renew. Sustain. Energy Rev. 2020, 121, 109669-109686.

[18] Jamalia, A.; Vanraes, R.; Hanselaer, P.; Van Gerven, T. Chem. Eng. Process.: Process Intens. 2013, 71, 43-50.

[19] Mishra, V. S.; Mahajani, V. V.; Joshi, J. B. Ind. Eng Chem. Res. 1995, 34, 2-48

[20] Lehr, J. H. Wiley's Remediation Technologies Handbook: Major Contaminant Chemicals and Chemical Groups. John Wiley & Sons, 2004, ISBN: 978-0-471-45599-8.

[21] Kaptijn, J. P. Ozone Sci. Eng. 1997, 19, 297-305.

[22] Fenton, H. J. H. J. Chem. Soc. 1894, 65, 899-911.

[23] Pignatello, J. J. Environ. Sci. Technol. 1992, 26, 944-951.

[24] Kiwi, J.; Pulgarin, C.; Peringer, P.; Gratzel, M. Appl. Catal. B: Environ. 1993, 3, 85-99.

[25] Pulgarin, C.; Kiwi, J. Chimia 1996, 50, 50-55.

[26] Zheng M., Xing C., Zhang W., Cheng Z., Liu X., Zhang Q.: Inorg. Chem. Commun 119, 2020, 108040-108047.

[27] Liu Ch., liu Y., Zeng S., Li Ch.: Appl. Surf. Sci. 544, 2021, 148886-148898.

[28] Pignatello, J. J.; Liu, D.; Huston, P. Environ. Sci. Technol. 1999, 33, 1832-1839.

[29] Ollis, D.; Al-Ekabi, H.; Eds. Photocatalytic Purification of Water and Air, Elsevier, New York, 1993.

[30] Zhang, Y.; Crittenden, J. C.; Hand, D. W.; Perram, D. L. Environ. Sci. Technol. 1994, 28, 435-442.

[31] Muruganandham, M.; Wu, J. J. Appl. Catal. B: Environ. 2008, 80, 32-41.

[32] Duran, A.; Monteagudo, J. M. Water Res. 2007, 41, 690-698.

[33] Muruganandham, M.; Swaminathan, M. Sep. Purif. Technol. 2006, 56, 101-107.

[34] Emamdoust A., La Parola V.,. Pantaleo G, Testa M. L., Farjami Shayesteh S., Venezia A. M.: J. Energ. Chem. 2020, 47, 1-9.

[35] Ramesh A., Tamizhdurai P., Mangesh V.L., Palanichamy K., Gopinath S., Sureshkumar K., Shanthi K.: J. Hydrogen Energ. 2019, 44 (47), 25607-25620.

[36] Fernández-Catalá J., Cazorla-Amorós D., Berenguer-Murcia Á.: Appl. Catal. A 2018, 564, 120-126.

[37] Rice, R. G. Ozone Sci. Eng. 1996, 18, 477-515.

[38] Song Y., Zhao Ch., Wang T., Kong Z., Zheng L., Ding H., Liu Y., Zheng H.: Water Res. 2021, 189, 116623-116632.

[39] Baxendale, J. H.; Wilson, J. A.; Trans. Farad. Soc. 1957, 16, 344-356.

[40] Song Y.L., Cui Ch.X., Liu Y.J.: J. Photochem. Photobiol. A Chem. 2016, 317, 68-71.

[41] Campus-Martin J. M., Blanco-Brieva G., Fierro J. L. G., Angew. Chem. Int. Ed. 2006, 45, 6962-6984.

[42] Dittmeyer, R.; Grunwaldt J. D.; Pashkova, A. Catal. Today 2014, 248, 149-155.

[43] Thenard, L. J. Ann. Chim. Phys. 1818, 8, 306-312.

[44] Goor G., Glenneberg J., Jacobi S.: Hydrogen Peroxide: Manufacture and Industrial Use for Production of Organic Chemicals, Springer, Netherlands 1992, ISBN 978-94-017-0984-2.

[45] Ranganathan S., Sieber V: Catalysts 2018, 8, 379-400.

[46] Apyari V.V., Terenteva E.A., Kolomnikova A.R., Garshev A.V., Dimitrienko S.G., Zolotov Y.A.: Talanta 2019, 202, 51-58.

[47] Ogata, Y.; Tomizawa, K.; Takagi, K. Can. J. Chem. 1981, 59, 14-18.

[48] Gogate, P. R.; Pandit, A. B. Adv. Environ. Res. 2004, 8, 553-597.

[49] Paul, S. M. M.; Aravind, K. U.; Pramod, G.; Aravindakumar, C. T. Chemosphere 2013, 91, 295-301.

[50] Guittonneau, S.; de Laat, J.; Dore, M.; Duguet, J. P.; Bonnel, C. Rev. Sci. Edu. 1988, 1, 85-91.

[51] Tuazon, E. C.; Aschmann, S. M.; Nishino, N.; Arey, J.; Atkinson, R. Phys. Chem. Chem. Phys. 2005, 7, 2298-2304.

[52] Glaze, W. H.; Kang, J.-W.; Chapin, D. H. Ozone Sci. Eng. 1987, 9, 335-352.

[53] Suty, H.; De Traversay, C.; Cost, M. Wat. Sci. Technol. 2004, 49, 227-233.

[54] Pignatello J. J., Oliveros E., MacKay A. Crit. Rev. Environ. Sci. Technol. 2006, 36, 1-84.

[55] Balachandran R., Zhao M., Dong B., Brown I., Raghavan S., Keswani M.: Microel. Eng. 2014, 130, 82-86.

[56] Bhattacharjee, S. Shah, Y. T. Rev. Chem. Eng. 1998, 14, 1-46.

[57] Shishida, K.; Echigo, S.; Yamada, H.; Matsui, S. J. Jpn. Soc. Water Environ. 1999, 22, 199-205.

[58] Gogate, P. R.; Pandit, A. B. Adv. Environ. Res. 2004, 8 501-551.

[59] EPA (US).: Ultraviolet Light Disinfection Technology in Drinking Water Application – An Overview. EPA 811-R96-002, 1996.

[60] Kosaka, K.; Yamada, H.; Shishida, K.; Echigo, S.; Minear, R. A.; Tsuno, H.; Matsui, S. Water Res. 2001, 35, 3587-3594.

[61] Combs, R.; McGuire, P. Ultrapure Water J. 1989, 6, 62-68.

[62] Sindelar, H. R.; Brown, M. T.; Boyer, T. H.; Chemosphere 2014, 105, 112-118.

[63] Krystynik, P.; Kluson, P.; Hejda, S.; Masin, P.; Tito, D. N. Water Environ. Res. 2014, 86, 2212-2220.

[64] Hofman-Caris, R. C. H. M.; Harmsen, D. J. H.; Beerendonk, E. F.; Knol, T. H.; Houtman, C. J.; Metz, D. H.; Wols, B. A. Chem. Eng. J. 2012, 210, 520-528.

[65] Flores M.J., Brandi R.J., Cassano A. E., Labas M.D.: Chem. Eng. J. 2012, 198-199, 388-396.

[66] Siegrist R. L., Crimi M., Simpkin T J., Eds. In Situ Chemical Oxidation for Groundwater Remediation, Springer, LLC 2011, ISBN: 978-1-4419-7825-7.

[67] Ayling G. W., Castrantas H. M.: Chem.Eng. 1981, 88, 79-82.

[68] Günsel A., Güzel E., Bilgicli A.T., Atmaca G.Y., Erdogomus A., Yarasir M. N.: J. Luminis. 2017, 192, 888-892.

[69] Ghazal B., Husain A., Ganesan A., Durmus M., Zhang X.F., Makhseed S.: Dyes and Pigments 2019, 164, 296-304.

[70] Trousil V., Cerny J., Korinkova R., Pummerova M., Mikulcova V., Herynkova M.: J. Photochem. Photobiol. A Chem. 2021, 405, 112985-112993.

[71] Kluson, P.; Drobek, M.; Strasak, T.; Krysa, J.; Karaskova, M.; Rakusan, J. J. Mol. Catal. A: Chem. 2007, 272, 213-219.

[72] Moser F. H., Thomas A. L.: Phthalocyanine Compounds. Reinhold Publ. Co., New York, Chapman and Hall, London, 1963, ISBN: 978-0278915954.

[73] Lang, K.; Mosinger, J.; Wagnerova, M. D. Chem. Listy. 2005, 99, 211-221.

[74] Derosa, C. M.; Crutchley, J. R. Coordin. Chem. Rev. 2002, 233, 351-371.

[75] Ogunbayo, T. B.; Antunes, E.; Nyokong, T. J. Mol. Catal. A: Chem. 2011, 334, 123-129.

[76] Gerdes, R.; Wohrle, D.; Spiller, W.; Schneider, G.; Schulz-Ekloff, G. J. Photochem. Photobiol. A: Chem. 1997, 111, 65-74.

[77] Oldham, T. C.; Phillips, D. J. Photochem. Photobiol. B: Biol. 2000, 55, 1619.

[78] Cerny, J.; Karaskova, M.; Rakusan, J; Nespurek, S. J. Photochem. Photobiol. A: Chem. 2010, 210, 82-88.

[79] Ishii, K. Coordin. Chem. Rev. 2012, 256, 1556-1568.

[80] Rychtarikova, R.; Kuncova, G. Chem. Listy. 2009, 103, 800-813.

[81] Dilber G., Durmus M., Kantekin H.: Dyes and Pigments 2019, 160, 267-284.

[82] Czaplicka, M. J. Hazard. Mater. 2006, 134, 45-59.

[83] D'Alessandro, N.; Liberatore, L.; Tonucci, L.; Morvillo, A.; Bressan, M. J. Mol. Catal. A: Chem. 2001, 175, 83-90.

[84] Tonucci, L.; Nicastro, M.; D'Alessandro, N.; Bressan, M.; D'Ambrosio, P.; Morvillo, A. Green Chem. 2009, 11, 816-820.

[85] Sharma, V. B.; Jain, S. L.; Sain, B. Tetrahedron Lett. 2003, 44, 383-386.

[86] Sorokin, A. B. Chem. Rev. 2013, 113, 8152-8191.

[87] Kluson, P.; Drobek, M.; Kalaji, A.; Zarubova, S.; Krysa, J.; Rakusan, J. J. Photochem, Photobiol. A: Chem. 2008, 199, 267-273.

[88] Kluson, P.; Drobek, M.; Krejcikova, S.; Krysa, J.; Kalaji, A.; Cajthaml, T.; Rakusan, J. Appl. Catal. B: Environ. 2008, 80, 321-326.

[89] Kluson, P.; Drobek, M.; Zsigmond, A.; Baranyi, J.; Bata, P.; Zarubova, S.; Kalaji, A. Appl. Catal. B: Environ. 2009, 91, 605-609.

[90] Kluson, P.; Drobek, M.; Kalaji, A.; Karaskova, M.; Rakusan, J. Res. Chem. Intermediat. 2009, 35, 103-116.

[91] Drhova, M.; Hejda, S.; Kristal, J.; Kluson, P. Proced. Eng. 2012, 42, 1365-1372.

[92] Hejda, S.; Drhova, M.; Kristal, J.; Buzek, D.; Krystynik, P.; Kluson, P. Chem. Eng. J. 2014, 255, 178-184.

[93] Bartels, O.; Wohrle, D.; Caro, J.; Wark, M. Stud. Surf. Sci. Catal. 2004, 154, 2884-2892.

[94] Mohamed, R. M.; Mohamed, M. M. Appl. Catal. A: Gen. 2008, 340, 16-24.

[95] Krystynik, P.; Kluson, P.; Hejda, S.; Buzek, D.; Masin, P.; Tito, D. N. Appl. Catal. B: Environ. 2014, 160, 506-513.